an electrolyte in contact with the porous coating and the anode[; and a], the container containing the anode and the electrolyte [that is in contact with the porous coating and the anode].--;

Claim 38 (Amended), line 1, delete "electrolytic";

Claim 39 (Amended), line 1, delete "electrolytic";

Claim 40 (Amended), line 1, delete "electrolytic".

REMARKS

In response to the Examiner's Action mailed January 24, 1994, Applicant amends his application and requests reconsideration. In this Amendment, claim 4 is cancelled so that claims 1, 5-12, and 37-40 remain pending and under examination.

In response to the Examiner's comments concerning the references AS and AW referred to in the Information Disclosure Statement, Applicant does not know the year of publication of those documents. However, those publications were published before the filing date of this application and Applicant considers them to be prior art publications.

Claims 1, 4-12, and 37-40 were rejected as indefinite with reference being made to particular language in claims 37 and 4. Claim 4 was also asserted to be confusing. In this Amendment, claim 4 is cancelled. Claim 37 is amended and provides antecedent basis for the term "inside surface". In addition, antecedent basis is provided for the term cathode in the amendment to claim 37. Applicant believes that there is no confusion in claim 37 concerning whether the electrolyte is in physical or electrical contact with the porous coating and the anode. As known to one of skill in the art, the electrolyte in a capacitor employing such an electrolyte must be in physical contact with the anode and cathode. It follows that, because an electrolyte is inherently electrically conducting, the electrolyte is also in electrical contact with the anode and the cathode comprising the porous coating. Thus, there is no ambiguity requiring further clarifying amendment of claim 37. The foregoing amendments and remarks overcome the rejections of the claims as to form.

A number of changes are made to the specification so that it does not refer to the invention as an electrolytic capacitor. The invention is a novel capacitor that might be most accurately referred to as a hybrid capacitor because it incorporates some elements found in electrolytic capacitors and some elements found in electrochemical capacitors. Thus, the word "electrolytic" is not precisely correct in referring to the novel capacitor. For that reason, both the specification and claims are amended to

refer to the invention merely as a capacitor.

Claims 1, 5, 7, 10-12, 37, 38, and 40 were rejected as unpatentable over Buice (U. S. Patent 3,531,693) in view of Beer (U. S. Patent 3,632,495). This rejection is respectfully traversed.

Buice describes an electrolytic capacitor including a metal container having an inside surface on which a film of metallic ruthenium is deposited. There is no suggestion in Buice that the metallic ruthenium is oxidized or is ruthenium oxide. In fact, because of the relatively low temperatures employed in the process described by Buice, it is apparent that no ruthenium oxide could be formed on the inside surface of he metal container. Oxidation of ruthenium in air requires a temperature approaching 400°C whereas the highest temperature mentioned by Buice is 125°C.

In order to meet the limitation of claim 37 describing a cathode including an oxide of a metal selected from a specified group of metals including ruthenium, reliance was placed upon Beer. However, Beer does not describe a capacitor of any kind. Instead, Beer is directed to electrolysis electrodes used in the production of chlorine and alkaline metals as well as the production of various compounds, such as chlorates, hypochlorites, persulphates, perborates, and other applications, such as the desalinization of water and in cathodic protection systems. Beer is not analogous prior art that can be applied in rejecting the

examined claims. The two-pronged test for determining whether a publication is analogous prior art as stated in In re Wood, 202 USPQ 171 (CCPA 1979) is still applied. The first test is whether a publication is within the field of the endeavor of the invention as defined by the claims being examined. If not, the second test is whether the publication is reasonably pertinent to the particular problem to which the invention is directed.

The field of the inventor's endeavor is electrical capacitors. Capacitors are used in electrical and electronic circuits for storing charge. By contrast, Beer is directed to the structure of a single electrode, used in combination with a counter electrode, in an electrolysis cell in which, typically, a compound is dissolved in a solvent. A flow of electricity between the electrode and the counter electrode results in a chemical reaction resulting in liberating one of the elements of the dissolved compound or producing another compound. This electrolysis process consumes the dissolved material and generally involves caustic or acidic materials that attack the electrolysis electrode. Beer is directed to an electrode that resists attack in the electrolysis process.

An electrolysis cell is substantially different from a capacitor because electrolysis does not involve the storage and retrieval of electrical charge. Instead, electrolysis involves the flow, not the storage, of electrical charge between the electrodes to produce a desired chemical reaction. Because of these

differences, it is readily apparent that Beer is not within the field of endeavor of the present invention.

The particular problem to which the invention is directed is the production of a capacitor having an increased energy storage density. In other words, for a particular volume, the problem to be solved is increasing the quantity of stored electrical charge. An allied problem solved in the invention is the avoidance of a low breakdown voltage in the capacitor having increased energy storage density. Pcapacitors, such as carbon double layer capacitors, that have relatively large storage densities are known in the art but suffer from low breakdown voltages. Other kinds of known capacitors with high energy storage densities, for example, pseudocapacitors, likewise suffer from low voltage breakdown. These problems are very different from the problem addressed by Beer and their solution is not suggested by Beer. Instead, Beer is directed to the production of long lasting electrolysis electrodes. Beer is directed to an electrode that involves no electrical charge storage so that the quantity of charge storage is irrelevant to any problem that might concern Beer. Likewise, in electrolysis, the voltage applied or sustained across an electrolysis cell is not limited nor controlled by a breakdown voltage. Rather, in electrolysis, the voltage applied to the cell is determined by the type and rate of the chemical reaction occurring within the cell. Beer can contain no information relating to the problem of maintaining an increased voltage across elec-

trodes without breakdown. For these reasons, Beer is not reasonably pertinent to the problem to which the invention is directed. Since Beer fails to meet either test of Wood, it is non-analogous art that should not have been applied in rejecting any of the pending claims.

Even if Beer were analogous prior art, it still would not suggest a modification of Buice to produce the claimed invention. In Buice, a metallic ruthenium layer covers the inside surface of the metallic casing of a capacitor. There is no suggestion in Buice that this metallic layer should be replaced with an oxide of a metal or a mixed oxide to achieve any particular advantage or improvement in performance. Beer is directed to the production of a durable electrolysis electrode and contains no suggestion for use of those electrodes in capacitors nor any advantage, other than extended lifetime in electrolysis, that could provide any basis or motivation for modification of Buice's cathode. Buice contains no suggestion that the ruthenium-coated capacitor case has any lifetime problem that might motivate one of skill in the art to search for a solution to such a problem in Beer or anywhere else. In fact, according to Buice in column 4, lines 59-69, capacitors employing the ruthenium metal coating have lifetimes as good as and even better than conventional capacitors. Thus, no motivation can be found in Buice and Beer for their combination.

At best, the Examiner is suggesting that, given Beer, it would be "obvious to try" Beer's electrode as the cathode of an electrolytic capacitor. However, "obvious to try" is not the test of obviousness mandated by 35 U.S.C. §103. Rather, the appropriate question is whether one of skill in the art would find some motivation in Buice or Beer for modifying Buice using some teaching from Beer. For all of the reasons discussed above, there is no such motivation for such a modification in either reference and, therefore, it would not be obvious to modify Buice with Beer. At worst, the Examiner is proposing to combine selected portions of Beer with Buice based upon knowledge of the invention. Because, for the reasons already discussed, there is no connection between the technologies of Buice and Beer, it is difficult to find any other basis for such a combination than a "hindsight" patentability analysis. Reconstruction of an invention from prior art references based solely on knowledge of the claimed invention has long been discredited as an inappropriate test of determining the patentability of a claimed invention.

The invention claimed in the present application is an important advance in the capacitor art, a well developed art. The inventor described his invention at the 14th Annual Capacitor and Resistor Technology Symposium (CARTS 94) during March of 1994. A copy of the inventor's paper is attached. In advance of the symposium, several journalists in the electronics industry obtained copies of the paper and published articles referring to

it. Copies of two of those articles are attached. One, from the Electrical Engineering Times describes the invention as "a unique new" hybrid capacitor. Another, from the Capacitor Industry Newsletter, describes the invention as providing a "quantum leap", a "design [that] could potentially ring in the first truly 'new' product in this industry for many, many years". The authors of these articles asked the inventor's permission to print these items before the CARTS 94 conference but the attached news articles were not solicited by the inventor nor was any of the language of the articles provided or suggested by the inventor. These descriptions of the invention as an unexpected, important development in the capacitor art by those working in the pertinent art provide additional indicia of the novelty and non-obviousness of the invention.

For all of the foregoing reasons, the invention as defined by independent claim 37, the only independent claim under examination, is not obvious in view of and is patentable over Buice and Beer.

Claims 6, 9, and 39 were rejected as unpatentable over Buice in view of Beer and further in view of Cannon (U. S. Patent 4,245,275). This rejection is respectfully traversed.

Claims 6, 9, and 39 are all dependent claims and Cannon was relied upon only as describing a capacitor with a sulfuric acid electrolyte. Applicant does not dispute that capacitors employing sulfuric acid as an electrolyte in combination with tantalum

anodes and cathodes is known in the art. However, since the rejected claims all incorporate the limitations of independent claim 37, the issue of patentability is whether Buice, Beer, and Cannon, in combination, might suggest the invention defined in claims 6, 9, and 39. For the reasons extensively described above, claim 37 is not obvious in view of the purported combination of Buice and Beer. There is no suggestion in Cannon for the elements of independent claim 37 that are missing from the primary and second references. Therefore, claims 6, 9, and 39 are patentable for the same reasons that claim 37 is patentable.

Claim 8 was rejected as unpatentable over Buice in view of Beer and further in view of Katzman (U. S. Patent 2,236,270). This rejection is respectfully traversed.

Katzman was cited as showing that it is known in the art to use an ammonium salt and glycol solvent as an electrolyte in a capacitor employing aluminum electrodes. However, since the rejected claim incorporates the limitations of independent claim 37, the issue of patentability is whether Buice, Beer, and Katzman, in combination, might suggest the invention defined in claims 6, 9, and 39. For the reasons extensively described above, claim 37 is not obvious in view of the purported combination of Buice and Beer. There is no suggestion in Katzman for the elements of independent claim 37 that are missing from the primary and secondary references. Therefore, claim 8 is patentable for the same reasons that claim 37 is patentable.

For each of the foregoing reasons, no claim now pending and under examination can be unpatentable in view of the publications relied on. Accordingly, a favorable Action on the merits is solicited.

Respectfully submitted,

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High Energy Density Electrolytic-Electrochemical Hybrid Capacitor

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Abstract

A novel electrolytic/ electrochemical capacitor has been developed that has five-times higher capacitance density than standard electrolytic devices. The capacitor is comprised of a pressed-sintered tantalum anode, formed Ta2O5 dielectric, aqueous electrolyte, and a metal oxide ceramic cathode. The properties of each constituent are discussed.

Electrical characteristics of a 480 µF, 200 V, 2.5 cc prototype capacitor are reported. Data presented include discharge capacitance, ac impedance, and frequency analysis. A volumetric energy density of 4 J/ cc was obtained for prototype devices.

Background

Electrolytic capacitors enjoy wide popularity because they are inexpensive, exhibit good electrical performance, and have high specific energy compared to other capacitor types in similar applications. For example, the energy density of high CV aluminum electrolytic capacitors (Mallory CGH) is on the order of 1 J/cc.

As the density and performance of active electronic devices increased, motivation developed to reduce the size of associated passive components. During the period which saw orders-of-magnitude reductions in size for active components, the energy density of electrolytic capacitors remained constant.

The first electrochemical capacitors, introduced by Sohio in the 1970s had an energy density of just over 2 J/cc (1.0 F, 5.5 V). Although this was a dramatic increase over electrolytic capacitors, applications of these devices have been limited by their relatively poor frequency response and low working voltage. These devices exploited the double-layer capacitance on high surface area carbon electrodes. Unlike capacitors using a dielectric, electrochemical capacitors with aqueous electrolyte have a maximum operating voltage limited to about 1 V/cell. This complicates the construction of practical high-voltage devices.

As presented to the 14th Capacitor & Resistor Technology Symposium 3/22/94
and published in Carts' 94 Proceedings.

Other types of electrochemical capacitors have been described in the literature. One such capacitor, based on the pseudocapacitance found on symmetric pairs of mixed-metal-oxide electrodes, promised further increases in energy density (perhaps to 5 or 10 J/cc), though it was bothered by the same problems of the carbon types. Additionally, the active materials were very costly. As a consequence, this technology has had little commercial impact.

The needed device was a higher energy density capacitor which had increased voltage capability and improved frequency response. The objective of this work was to develop, build, and test such a device. The resulting device, combining the characteristics of both electrolytic and electrochemical capacitor types, met the objective.

Discussion

An electrolytic capacitor can be simply modeled by the circuit shown in Figure 1. It is equivalent to distinct anode and cathode capacitors connected in series by the electrolyte. The dielectric is usually a non-conductive oxide of the metal which forms the electrode. These devices are usually asymmetric, that is, they have a preferred arrangement of anode and cathode. The thickness of the dielectric on the anode sets the working voltage of the device. The thickness of the cathode dielectric sets the reverse voltage capability, but does not contribute to the device working voltage.

Figure 1. Electrolytic capacitor circuit model.

In commercial aluminum and tantalum electrolytic capacitors, the dielectric is thinner on the cathode than the anode. Most manufacturers use the highest specific surface area aluminum foils or tantalum powders available for the cathode because these materials are capable of the low voltage formations needed for the cathode dielectric. Typically, lower specific surface area materials are used for the anode because they are capable of the much higher voltage formations needed for the anode dielectric. The thinner dielectric and increased surface area of the cathode cause the cathode capacitance to be higher than the anode capacitance. The effect of changing the relative capacitances of the anode and cathode on device capacitance is readily apparent remembering that

$$1/Ct = 1/Ca + 1/Cc \qquad (1)$$

where Ct is device capacitance, Ca is anode capacitance, and Cc is cathode capacitance. If Ca = Cc, then Ct = ½Ca. If either Ca >> Cc or Cc >> Ca, the device capacitance, Ct, will approach the smaller of Ca or Cc.

Mixed-metal-oxide (MMO) electrochemical capacitors have high surface area electrodes characterized by very high specific capacitance, on the order of 200 to 500 μF/cm² of

real surface area [1]. Because they employ no dielectric, the working voltage of the capacitor cannot exceed the breakdown potential of the electrolyte, which is about 1.2 volts for aqueous systems. This is a real disadvantage because high-voltage devices need multiples of cells stacked in series. This series arrangement, by extension of equation (1) results in a severe capacitance penalty.

Figure 2 compares the volumetric energy density predicted for the new capacitor (HI-Q) with actual values for commercial aluminum foil and tantalum wet slug devices. As shown, significant improvements in energy density are expected for the HI-Q device. At 100 V for example, the HI-Q energy density is five-times greater than the aluminum electrolytic value.

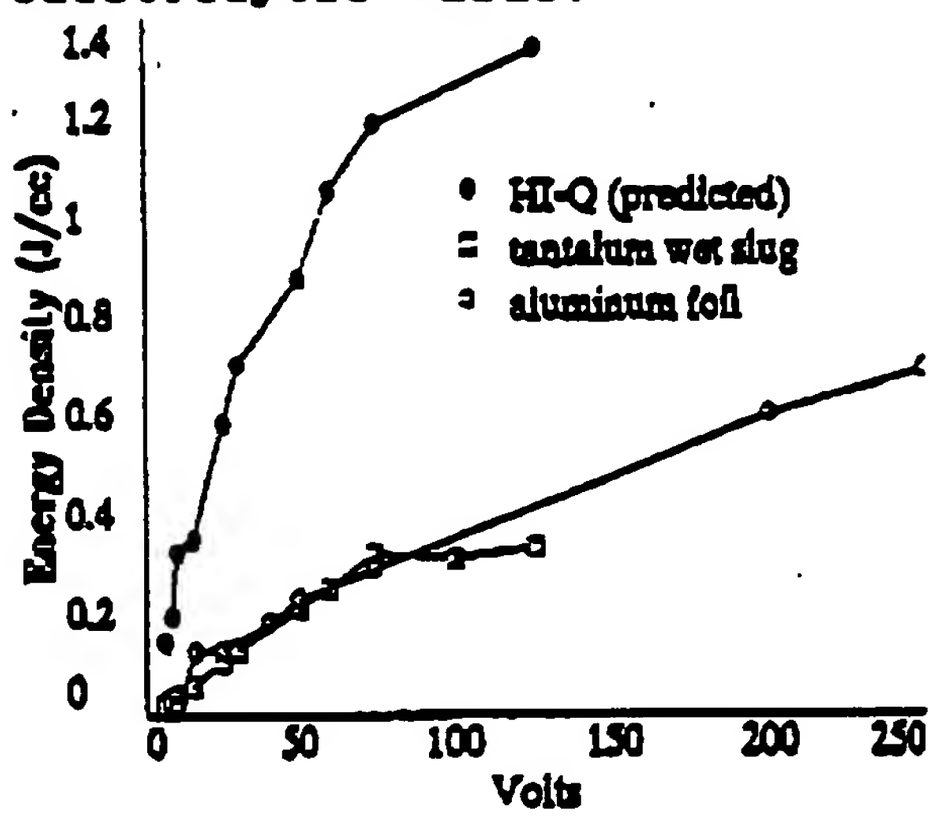


Figure 2. Energy density vs. Voltage for various capacitor types.

In order to fully exploit the capability of the MMO electrode materials, it is essential to eliminate the voltage limitation caused by electrolyte breakdown. This can be accomplished by limiting the voltage drop across the electrolyte/ MMO interface to less than the breakdown voltage. Our approach was to add a dielectric in series with the electrolyte. The resulting cell voltage profile is shown in Figure 3. This keeps the voltage drop at the cathode electrolyte interface below the electrolyte breakdown potential.

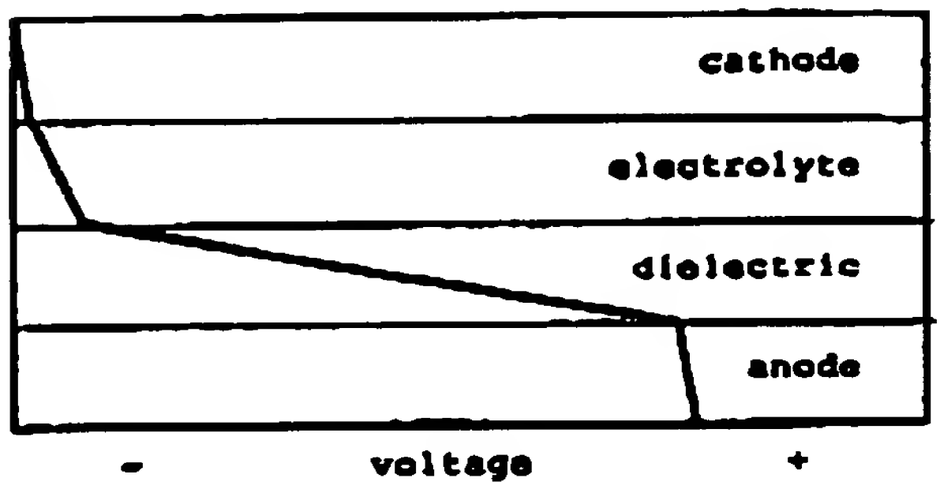


Figure 3. Schematic of cell voltage profile.

When composed of a non-conductive metal oxide, this dielectric is most stable on the anode of the cell. Substituting a MMO electrode deposited on foil for the aluminum or tantalum foil cathode in those capacitors would provide some improvement in energy density because the cathode capacitance would be increased without requiring additional volume. Significant improvement in capacitance density can be gained by changing from a foil to a sintered powder anode.

Prototype Construction

The prototype was targeted for an application requiring an energy density of 4J/cc and a working voltage of 215 V/cell.

The device design had a total of four series-connected cells, each with a capacitance of 480 µF. The total volume available for the packaged, high-reliability device was only 11 cc.

The anode was made from high-capacitance-density, high-purity, commercially available tantalum powder, pressed and sintered using standard methods. Formation of the tantalum pentoxide dielectric was done electrochemically in the usual way. This yielded a high-specific-surface-area porous electrode pellet with integral dielectric coating.

The MMO cathode was prepared on titanium foil according to a specific recipe developed to yield electrodes with a capacitance of about 6,000 µF/cm² of geometric area. The separator was a commercially available paper-based material. A suitable aqueous electrolyte was used.

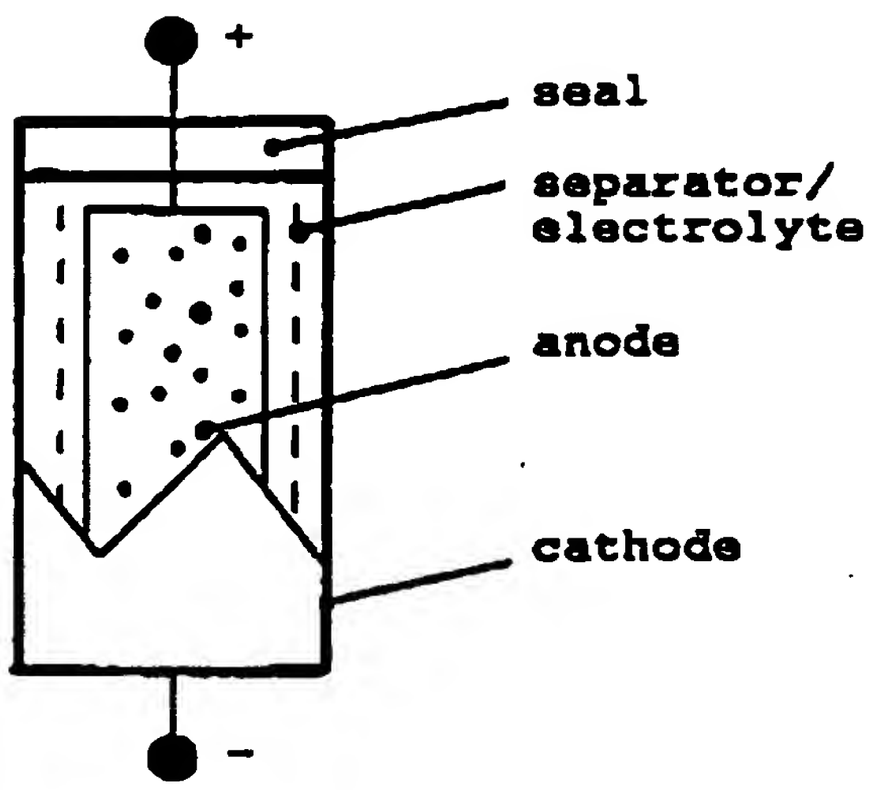


Figure 4. Schematic view of the prototype.

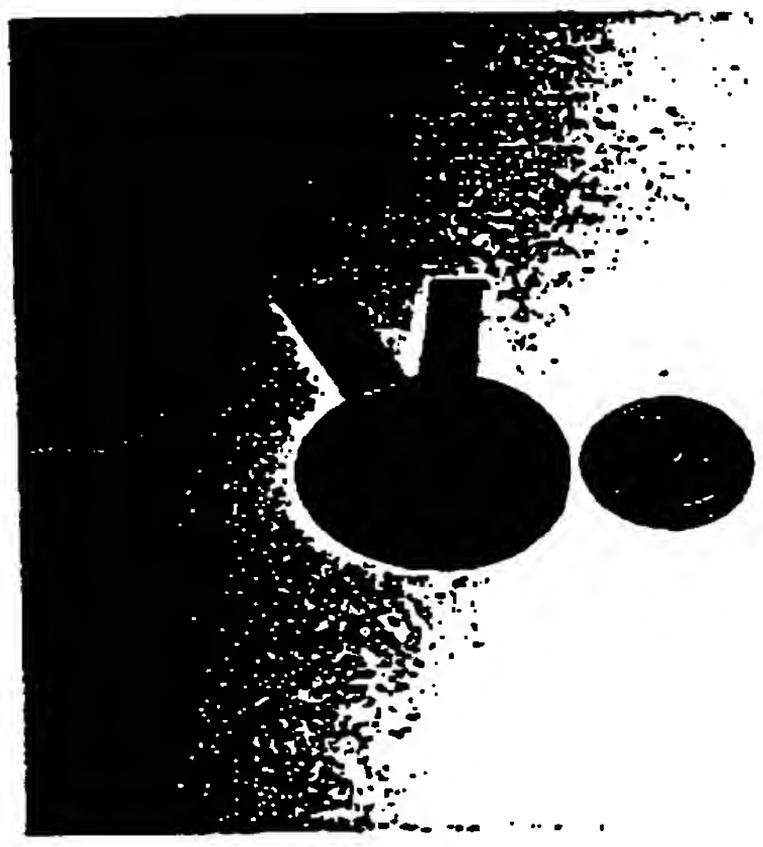


Figure 5. Photograph of the prototype.

Tests and Results

Several of the 215 V, 480 µF cells were constructed as described. Electrical properties were evaluated by fixed-resistance discharging, constant-current charging, ac impedance spectroscopy, and ac bridge measurements.

For an ideal capacitor discharged into a fixed resistance, the capacitance can be derived from the formula

$$V(t) = Vo\, e^{-t/RC} \qquad (2)$$

where Vo is the initial capacitor voltage, R is the fixed resistance, C is the capacitance, and V(t) is voltage as a function of time, t.

When t = T = RC, the voltage V(t) = 0.368 Vo. Capacitance taken at this time is referred to as the one-time-constant capacitance. 1 T and .25 T capacitance values are reported in Table 1. The difference in values reported at 1 T and .25 T indicate non-ideal behavior. Capacitance

is less than ideal for shorter discharge times.

For an ideal capacitor charged at a constant current, the capacitance is

$$C = It/V(t) \qquad (3)$$

where I is the current, V(t) is the voltage as a function of time, t. These numbers, for I = 10 mA, and t = 5 s. are reported in Table 1.

The values for leakage current (Il) listed in Table 1 were measured after a charge time of 15 m at 215 V with an ammeter in series with the charging circuit.

Measurements of ESR and capacitance were made with a GenRad model number 1658 Digibridge. Results are shown at 120 Hz and 1kHz. Again, differences in the values between one frequency and the other are due to non-ideal behavior.

Figure 6 shows the measured energy density of a single prototype device constructed for a working voltage of 215 V. The data were collected at various points by charging the device, then discharging into a 10 Ω resistor, calculating a 1 T capacitance, and using that in figuring the energy density. This procedure was repeated at each voltage reported.

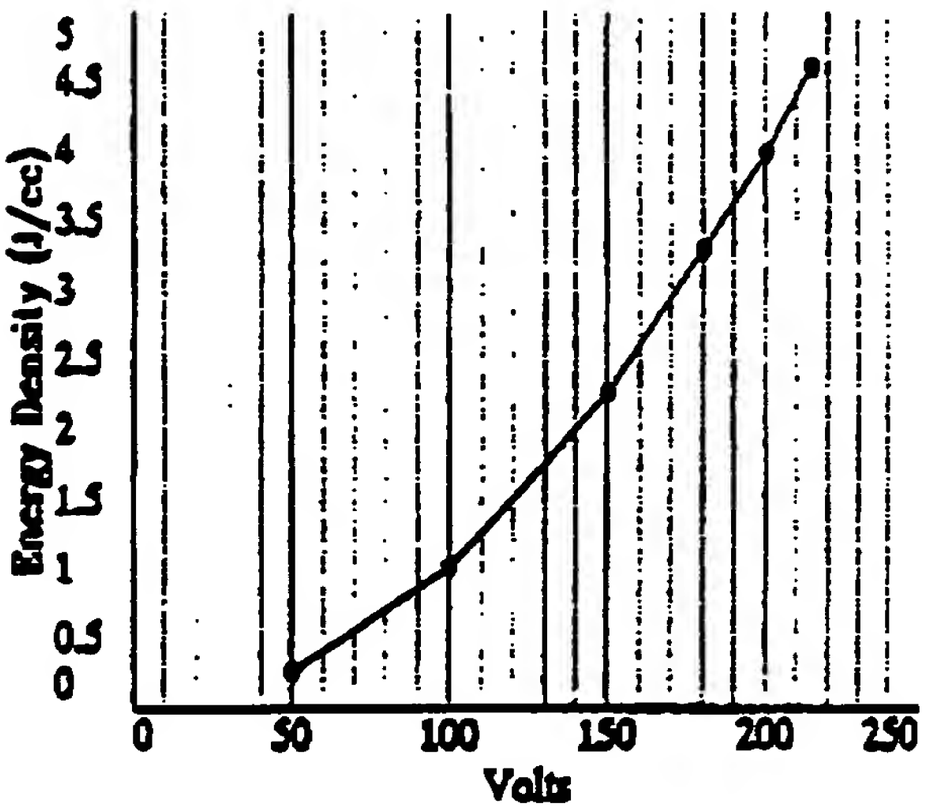


Figure 6. Energy density vs. Voltage for the HI-Q prototype.

The capacitance of this prototype did not vary significantly with voltage, as shown in Figure 7.

Table 1. Property Measurements

Part	Capacitance and method (μF)					ESR and method (Ω)			Il (μA)	Energy (Joules)
	A	B	C	D	E	D	E	F		
1	606	514	313	250	469	0.92	1.29	.238	114	11.3
2	541	470	249	226	429	0.99	1.37	.287	52	10.3
3	575	502	249	241	445	0.94	1.30	.287	82	11.0

Key to methods;
A. Constant-current charge
B. 10 Ω discharge, 1 T
C. 10 Ω discharge, .25 T
D. ac bridge, 1 kHz
E. ac bridge, 120 Hz
F. 10 Ω discharge
*energy calculation based on method B capacitance.

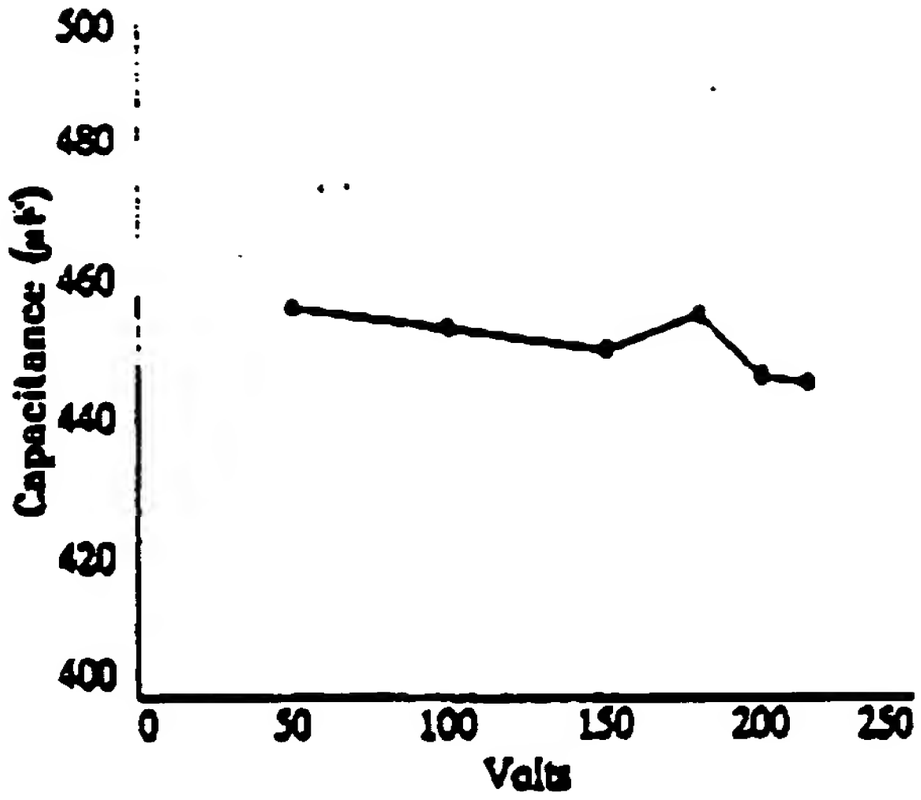


Figure 7. 1T Capacitance vs. Voltage for the prototype.

The non-ideal behavior can be examined in further detail using ac impedance spectroscopy. Figure 8 is a Nyquist plot giving the reactance vs. resistance over the frequency range of 79 Hz to 63 kHz for one of the prototype capacitors. This data was obtained using a Schlumberger Solartron 1260 frequency response analyzer with a 1.5 V bias and a 10 mV ac signal. The plot for an ideal capacitor is a straight vertical line intersecting the x-axis at the ESR value. The non-ideal 45° angle in the high frequency region is typical of devices with porous electrode structures, and was expected on this prototype.

Figure 9 presents the same impedance data in a different format, that is, a resistor-capacitor series combination. Electrical properties over the range in frequency of 1 Hz to 10 kHz are shown. The capacitance was flat within 10% to a frequency of about 200 Hz, where it rolls off sharply.

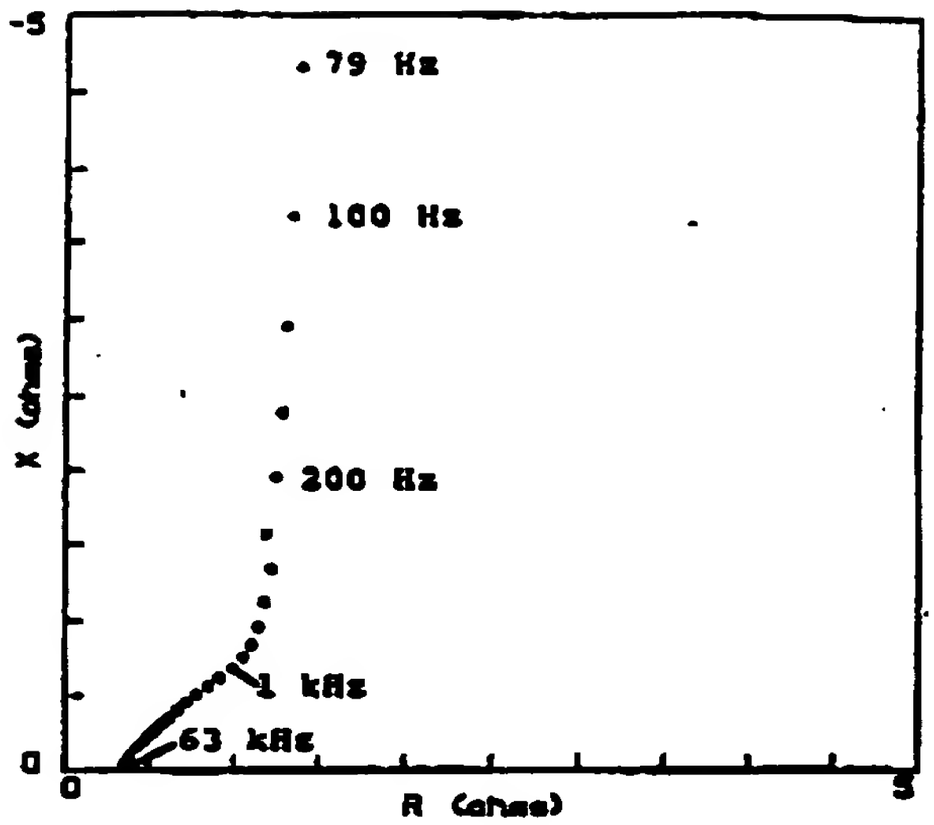
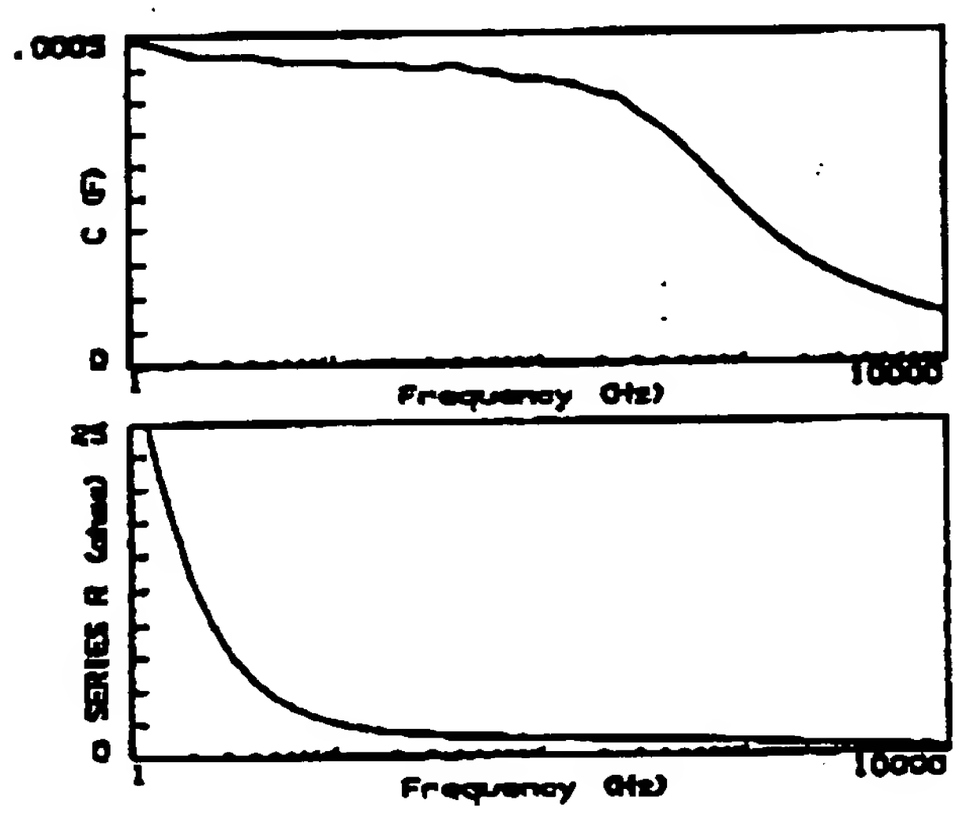


Figure 8. Nyquist Plot for the HI-Q prototype.

Figure 9. Electrical performance vs. Frequency.



Conclusion

The combination of mixed metal oxide cathodes and tantalum pellet type anodes yielded a device with very high energy density. The energy density of the prototype device was in excess of 4 J/cc at 215 V. This exceeds that of commercial electrolytic capacitors by a factor of five.

Work needs to be done and is ongoing to optimize the performance of these hybrid devices by improving their frequency response. Improved tantalum powders are being investigated, and modifications to the basic cathode recipe explored.

Reference

[1] B.E. Conway, "Some Basic Principles Involved in Supercapacitor Operation and Development", Proc. 3rd Int. Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, Florida (Dec. 6-8, 1993).

PASSIVE ACTIVITY

By Glenda Derman

Carts to carry papers, products

A unique new "hybrid" capacitor, combining tantalum and mixed-metal-oxide pseudo-capacitor technologies, is said to have the highest volumetric energy density available for its size. Details of this new technology and other information on capacitors, resistors and magnetic components will be presented at the annual Capacitor and Resistor Technology Symposium (Carts), March 21-24, at Jupiter Beach Resort, Jupiter, Fla. Seminars and technical and product sessions will be given by suppliers and users and will cover military and commercial passive components. Technical papers will cover topics on new design and developments, reliability and quality, testing and analysis, and materials and processes.

David Evans, engineering manager at Evans Co. (East Providence, R.I.), developer of the "hybrid" capacitor, will describe this new technology at Carts. Dubbed Hi-Q, the new capacitor, currently an engineering prototype, is said to have a capacitance density five times higher than standard electrolytic capacitors, up to 4 joules/cm³. It also has a much faster discharge rate than electrochemical capacitors. The surface-mountable Hi-Q, a disk 1¼ inches in diameter and one-tenth of an inch thick, handles up to 215 V and 480 μF. The capacitor comprises a pressed-sintered tantalum anode, a phosphoric acid electrolyte and a metal-oxide ceramic cathode. Applications include use in implantable defibrillators as well as replacements for aluminum electrolytics where smaller size is needed.

Electronic Engineering Times
CA
2/24/94

capacitor industry NEWSLETTER

Bi-monthly news for the film capacitor trade and allied dielectric marke

Volume IV, Issue 2 March-April 1994 ISSN# 1056-6813

ELECTROCHEMICAL WEDS ELECTROLYTIC

On the heels of last month's Newsletter special report on Electrochemical (Double Layer) Capacitors, comes word of a new hybrid development by Evans Co., of East Providence, RI. Details will have to await the paper to be presented Tuesday, March 22 at the CARTS conference in Jupiter, FL by David Evans. The paper is titled "High Energy Density Tantalum Electrochemical Hybrid Capacitor." Advance info describes a novel tantalum anode, metal-oxide ceramic cathode device with an aqueous electrolyte.

Although tantalum is involved in this study, work is being sucessfully done with aluminum as well. Early results for the Evans "Hi-Q" design show energy density increases of as much as five times that of tantalum or aluminum capacitors of the same volume, but with some work yet to be done in the area of frequency response. Powder forms of dielectric appear to be most applicable, indicating little opportunity to apply the technology with significant savings in foil or metallized film designs. Nonetheless, with such a quantum leap in the offing, this design could potentially ring in the first truly "new" product to this industry for many, many years.

ELECTROCHEMICAL MARKET STUDY

While we're on the subject of EC's, Dr. Sumner ("Shep") Wolsky of Ansum Enterprises and Richard Wiseoker of Wiseoker Associates have collaborated on a major worldwide Technology and Market Study of Electrochemical Capacitors. The $1650 volume covers history, theory, technology, R&D programs, market sizes, applications, manufacturers and component developers, performance data, trends, and over 1,500 patent references and 490 literature citations. For those buying the Study, also available for $250 is a computer disc for the patent and literature references.

Potential markets worldwide reportedly could total hundreds of millions of dollars. For those companies wanting to keep a pulse on possibilities for EC's or hybrids such as mentioned above, the Study is about the only comprehensive overview available. For info, call 407-338-8727, or Fax at 407-338-6887.